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INTERMOLECULAR POTENTIAL AND PROPERTIES OF ARGON

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ABSTRACT. By utilising the recent compressibility data, the potential field of argon has been determined on the Lennard-Jones (12·6) and (9:6) models. The force constants thus determined on the L-J (12·6) model give a better correlation of the various properties of argon than those obtained previously. A consideration of the equilibrium properties of argon lends support to the suggestion of Kihara that the potential bowl of the spherical molecules should be wider than that given by the L-J (12.6) model

INTRODUCTION

Considerable progress has already been made in correlating the various bulk properties of molecules and particular success has been achieved in the case of spherical molecules. One of the most common forms of the intermolecular potential used for this purpose is the Lennard-Jones ($n : m$) potential

$$\phi(r) = \epsilon \left[\frac{m}{n-m} \left(\frac{r_m}{r} \right)^n - \frac{n}{n-m} \left(\frac{r_m}{r} \right)^m \right] \qquad \ldots \quad (1)$$

where r is the distance between the two molecules and ϵ is the potential minimum at $r = r_m$. The quantity r_m is related to σ_n, the value for which $\phi(r) = 0$, by the relation

$$\sigma_n = r_m \left(\frac{m}{n} \right)^{\frac{1}{n-m}} \qquad \ldots \quad (2)$$

Theoretical considerations lead us to assume $m = 6$, but it is impossible to fix n from theory and it is usual to determine n from best empirical fit.

Even for spherical molecules, there remains some uncertainty about the best value of the index n. Several workers, Hirschfelder, *et al.* (1948), Srivastava and Madan (1953*a*, 1953*b*) and others have shown that the transport properties can be represented reasonably well with $n = 12$. Unfortunately due to difficulty in evaluating the complicated collision integrals for the transport properties, these have till now been evaluated only for $m = 6$, $n = 12$ (Hirschfelder, *et. al.*, 1954) and for $m = 4$, $n = 8$ (Clark-Jones, 1940).

It has been found that amongst the equilibrium properties the second virial coefficient $B(T)$ is rather insensitive to the form of potential chosen. The reason

for this may be found in the recent work of Kellar and Zumino (1959) which shows that $B(T)$ alone can determine only the repulsive part and the width of the intermolecular potential as a function of its depth. So it appears that from a consideration of $B(T)$ data at sufficiently high temperatures (where the repulsive part of the potential is more important), it should be possible to find the best value of n. Unfortunately, no such data exist. A serious disadvantage in using the third virial coefficient, $C(T)$ (which is sensitive to the potential form chosen), for determining the intermolecular potential is the difficulty of obtaining accurate values of $C(T)$, unless the compressibility data are very accurate. However, Bahadur and Madan (1960) have tried to obtain the force parameters on the $L-J$ (12 : 6) potential from $C(T)$ data by drawing smooth curves. Very recently, Guggenheim and McGlashan (1960) have obtained a five parameter potential for argon by utilising mainly the various crystal properties. It has however been shown by Jansen and McGinnies (1956) that in the crystalline state the assumption of pairwise additivity of the molecular forces is not strictly valid. The three-body long range forces in a crystal have been found to contribute a sizeable portion of the total Van der Waals interaction energy which becomes greater, the heavier the atom and the higher the density of the crystalline medium. Consequently, the treatment of Guggenheim *et. al.*, which is based on two-body forces, is somewhat uncertain.

Kihara (1953, 1955), from a consideration of $B(T)$ and $C(T)$ values suggested that at least for the spherical molecules, the potential bowl should be wider than that given by $L-J$ (12 : 6) potential, and $L-J$ (9 : 6) model might give better representation of the various molecular properties. However, some of the $C(T)$ values used by Kihara were not very reliable. Other workers Hirschfelder, *et al.*, (1954), Beattie (1952) and Michels (1958), have also found that the $L-J$ (12 : 6) potential is incapable of giving a completely satisfactory representation of the various equilibrium properties and have suggested that the discrepancies may be due to incorrectness of the potential form. It appears therefore that Kihara's suggestion requires further investigation. For this purpose we have chosen to consider the case of argon for which compressibility and other experimental data exist in the literature in the hope that a thorough consideration of various properties of argon may clear up some of the uncertainties. Attempts have also been made to get a set of force constants on the $L-J$ (12 : 6) model which will give a better correlation of the various properties of argon than that obtained hitherto.

DETERMINATION OF THE PARAMETERS

We have followed the procedure of Whalley and Schneider (1955) in fitting the experimental second virial data to the Lennard-Jones (12 : 6) and (9 : 6) potentials. The data used are those recently published by Michels *et al.* (1958) together

with their earlier determinations (1949) in the temperature range from −150°C to +150°C. The second virial coefficient $B(T)$ may be written as

$$B(T) = \rho B^*(T^*) \qquad \ldots (3)$$

where ρ is a constant depending on σ and $B^*(T^*) = B(T)/B(T)_{rig.sph.}$ The tables of B^* as a function of T^* have been obtained for the $L-J(12:6)$ model by Hirschfelder, *et al* (1954) and for $L-J$ (9 : 6) model by Epstein and Hibbert (1952). First the parameter ρ (which gives σ) and ϵ/k have been obtained approximately by following the graphical procedure of Lennard-Jones (1924). In order to determine ρ and ϵ/k more accurately the method of least squares (Deming 1943) has been applied as follows :

Let the approximate values of ρ and ϵ/k determined graphically be ρ_0 and $(\epsilon/k)_0$ and

$$\epsilon/k = (\epsilon/k)_0 - K \qquad \ldots (4)$$

$$\rho = \rho_0 - L \qquad \ldots (5)$$

where K and L are small correction terms. Then the normal equations for computing the correction terms are written as

$$\Sigma(KF_{\epsilon/k} + LF_\rho + F_0)F_\rho = 0 \qquad \ldots (6)$$

$$\Sigma(KF_{\epsilon/k} + LF_\rho + F_0)F_{\epsilon/k} = 0 \qquad \ldots (7)$$

with

$$F_0 = B(T) - \rho B^*(T^*)$$

$$F_{\epsilon/k} = -[\rho/(\epsilon/k)] \cdot T^* \left(\frac{dB^*}{dT^*}\right)$$

$$F_\rho = B^*(T^*).$$

TABLE I

Parameters on $L-J$ (12 : 6) and (9 : 6) potentials

Authors	L-J (12:6) model		L-J (9:6) model	
	σÅ	ϵ/K°K	σÅ	ϵ/K°K
Present work	3.418	120.23	3.584	89.59
Michels, *et al.* (1949)	3.405	119.8	—	—
Whalley and Schneidor (1955)	3.409	119.49	3.567	89.64
Hirschfolder, *et al.* from viscosity (1954)	3.418	124	—	—
Bahadur and Madan (1960)	3.419	120.5	—	—

Here F_0, $F_{\epsilon/k}$ and F_ρ are to be calculated using the absolute values $(\epsilon/k)_0$ and ρ_0. Eqs. (6) and (7) are then solved for K and L. If the difference between $(\epsilon/k)_0$ and ρ_0, and ϵ/k and ρ comes out to be more than a few percent the fitting is done by using better approximations.

The force constants thus determined on $L-J$ (12 : 6) and (9 : 6) models are shown in Table I, together with the values obtained by other workers.

COMPARISON WITH EXPERIMENT

(*a*) *Equilibrium Properties*

(i) *Second Virial and Third Virial Coefficients*

The experimental and calculated values of second virial coefficient $B(T)$ and the third virial coefficient $C(T)$ on Lennard-Jones (12 : 6) and (9 : 6) models are shown in Table II. For $B(T)$ it is not possible to determine the superiority of the $L-J$ (12 . 6) or the $L-J$ (9 : 6) potential over the other. It is, however, to be noted that Michels, *et al.* (1958) could not fit their $B(T)$ data at lower temperatures on the $L-J$ (12 : 6) models with the force constants previously determined by them (1949). It will be seen that with the force constants deter-

TABLE II

Experimental and calculated values of $B(T)$ and $C(T)$ on the $L-J$ (12 . 6) and $L-J$(9 · 6) models

T °K	B(T) (c.c./mole)				C(T) (c.c./mole)^2		
	Expt.	L-J (12:6) calc.	L-J (12.6) from Michels *et al.*	L-J (9·6) calc.	Expt.	L-J (12:6) calc.	L-J (9:6) model
133.2	−107.98	−106.79	−104 95	−104.79	2656	1426	1976
138.2	−100.88	− 99 69	− 98.13	− 98.04	2418	1478	1964
143.2	− 94.43	− 92.86	− 92.22	− 92 19	2417	1503	1943
148.2	− 88.45	− 87.95	− 87.36	− 86.77	2357	1505	1913
150.7	− 85.64	− 85.34	− 83.68	− 84.20	2313	1504	1899
153.2	− 82.97	− 82.81	− 81.26	− 81.79	2278	1499	1882
163.2	− 73 25	− 73.31	− 72.23	− 72 77	2104	1468	1810
173 2	− 65.21	− 65.63	− 63.68	− 65 05	2015	1416	1740
188.2	− 54.83	− 55.40	− 54.16	− 55.11	1791	1336	1637
203.2	− 46.83	− 47 14	− 45.95	− 46.93	1711	1255	1571
223 2	− 37.43	− 38.36	− 37.27	− 37.91	1541	1175	1451
248.2	− 28.57	− 30.61	− 28.46	− 28.96	1365	1085	1340
273.2	− 21.45	− 21 95	− 21.49	− 21.92	1270	1020	1279
298.2	− 15.75	− 15.83	− 15.93	− 15.98	1160	977	1241
323 2	− 11.24	− 11.65	− 11.16	− 11.38	1130	935	1176
348.2	− 7.25	− 7.48	− 7.28	− 7.36	1040	905	1139
373.2	− 4.0	− 4 10	− 3.98	− 3.94	1000	883	1110
398.2	− 1.18	− 1.34	− 1.14	− 1.046	970	866	1084
423.2	+ 1.38	+ 1.23	+ 1.31	+ 1.34	880	852	1062

mined in this paper, the low temperature $B(T)$ values of argon can also be represented satisfactorily on the $L-J(12\,.\,6)$ model.

The agreement between the experimental and the calculated values of $C(T)$ is not good either for the $L-J$ (12 : 6) or $L-J$ (9 : 6) potential, but is definitely better on $L-J$ (9 : 6) model.

(ii) *Joule-Thomson coefficient*

The Joule-Thomson Coefficient at zero pressure μ^0 may be written on the $L-J$ (12 : 6) model as

$$\mu^0 C_p^0 = b_0(B^*_1 - B^*) \qquad \ldots \quad (8)$$

TABLE III

Experimental and the calculated values of the J—T coefficient of argon at zero pressure in °C atm^{-1}

T °K	$\mu^0 \times 10^3$ Expt. (a)	$\mu^0 \times 10^3$ on the L-J (12;6) model	$\mu^0 \times 10^3$ on the L-J (9:6) model
123.2	1.750	1 648	1 527
137.7	1.293	1.386	1 311
148.2	1 075	1.217	1.155
160.7	0.935	1 070	1 026
173.2	0 835	0 988	0 9022
185.7	0.756	0.884	0.8034
198.2	0.695	0 736	0.7211
223.2	0 578	0 632	0 587
248.2	0 4905	0.522	0.492
273.2	0.418	0.445	0.419
298 2	0.360	0.388	0.362
323.2	0.312	0.330	0.314
348.2	0 270	0 304	0 2745
373 2	0 236	0.245	0.239
398.2	0.204	0.214	0.207
423.2	0.178	0.186	0 181
473.2	0.134	0.140	0.129

(a) J. R. Roebuck and H. Osterberg, (1934)

where C_p^0 is the zero pressure value of the molar specific heat, $b_0 = \frac{2}{3}\pi N\sigma^3$ and $B_1^* = T^* \cdot \frac{dB^*}{dT^*}$. The B^*_1 and B^* have been tabulated as a function of T^* (Hirschfelder *et al.*, 1954).

On the $L-J$ (9 : 6) model Epstein and Hibbert (1952) have calculated the values of B^* as a function of $1/T^*$. From these tables the values of B^* and B^*_1 as functions of T^*, required for calculating $\mu^0 C_p^0$ were obtained graphically. The values thus obtained are given in appendix which may be utilized for the calculation of μ^0 on the $L-J$ (9 : 6) model. The experimental and the calculated values of μ^0 on different molecular models are given in Table III. It is interesting to note that Hirschfelder (1938) could not fit the experimental μ^0 data for argon on the $L-J$ (12 : 6) model Table III shows that the $L-J$ (9 . 6) potential gives a better agreement with the experimental values of μ^0 than the $L-J$ (12 : 6) model.

(iii) *Crystal properties*

The heat of sublimation, $\Delta H_v(0)$ and the lattice spacing, R, both at 0°K are simply correlated with the inter-molecular potential provided the substance crystallises in the cubic system. The equations for the lattice spacing including the effect of zero point energy have been given by Corner (1948) for $(n : 6)$ potential which have been reduced for the $L-J$ (12 . 6) and $L-J$ (9 · 6) potential as follows :

For the $L-J$ (12 · 6) potential,

$$C_0 = 2C_{12}\left(\frac{\sigma}{R}\right)^6 + \left\{\frac{h^2}{8\pi^2 m\sigma^2}\right\}^{\frac{1}{2}} \cdot \frac{77C_{14}\left(\frac{\sigma}{R}\right)^6 - 10C_8}{\left\{22C_{12}\left(\frac{\sigma}{R}\right)^{10} - 5C_8\left(\frac{\sigma}{R}\right)^4\right\}^{\frac{1}{2}}} \quad \ldots \quad (9a)$$

and for $L-J$ (9 : 6) potential

$$C_0 = C_9\left(\frac{r_m}{R}\right)^3 + \left\{\frac{h^2}{3\pi^2 m\epsilon r_m^2}\right\}^{\frac{1}{2}} \cdot \frac{11C_{11}\left(\frac{r_m}{R}\right)^3 - 5C_6}{\left\{4C_{11}\left(\frac{r_m}{R}\right)^7 - \frac{5}{2}C_6\left(\frac{r_m}{R}\right)^4\right\}^{\frac{1}{2}}} \quad \ldots \quad (9b)$$

where r_m = value of r at potential minimum

h = Planck's constant

m = mass of the molecule

and C_n for $n = 1, 2$, etc. are numerical constants calculated by Lennard-Jones and Ingham (1925). Using the force constants determined in the present paper, the value of R was evaluated from Eqn. (9). This value of R was used for calculating the $\Delta H_v^{(0)}$ with the help of equation given below for $(n : 6)$ potential,

$$\Delta H_v^{(0)} = \frac{1}{2} N\epsilon \left[6C_n \left(\frac{r_m}{R}\right)^n - nC_6 \left(\frac{r_m}{R}\right)^6 \right] / (n-6) \qquad \ldots (10)$$

The values of $\Delta H_v^{(0)}$ and R thus obtained together with the experimental values are given in Table IV. It is to be noted that the crystal data cannot give any definite information about the suitability of any particular form of potential as it has been shown by McGinnes and Jansen (1956) that the assumption of the additivity of molecular force is not possibly valid in the crystalline state. Consequently, equations (9) and (10) which are based on this assumptions are somewhat uncertain.

TABLE IV

Experimental and calculated values of $\Delta H_v^{(0)}$ and R for argon

Authors	$H_v^{(0)}$ in cal./mole			R in Å		
	Expt	Calculated		Expt.	Calculated	
		L-J (12·6)	L-J (9:6)		L-J (12:6)	L-J(9:6)
Present work	[a] 1998±40	2010	1722	[b] 3 81	3.73	3 908
Whalley and Schneider		2033±6	1718±5		3.767	3.929

(a) Whalley and Schneider, (1955)
(b) Simon and Von Simon, (1924)

(*b*) *Transport properties*

(i) *Viscosity*

The experimental and the calculated values of viscosity of argon on $L-J$ (12 . 6) model have been given in Table V. The agreement of calculated values with the experimental data is better than that obtained by using Michels' force constants. It has long been known that the high temperature viscosity data of argon cannot be represented well by the $L-J$ (12 . 6) potential. This may be due to the increasing importance of the repulsive part of the intermolecular potential at high temperature which should vary exponentially rather than obey an inverse power law.

(ii) *Thermal conductivity*

The experimental and calculated values of the thermal conductivity of argon is given in Table VI. The theoretical values were calculated to the first approxi-

TABLE V

Experimental and calculated values of viscosity of argon (in 10^{-7} gm/cm.sec)

T °K	Expt.	Calculated from our constants	Calculated from force constants of Michels, (*et al*).	Calculated from force constants from viscosity	Ref for Expt. data
80	688	660	666	649	a
120	993	997	1005	979	a
160	1298	1319	1332	1300	a
200	1594	1620	1636	1601	a
240	1878	1902	1920	1882	a
280	2145	2166	2182	2143	a
298	2228	2274	2279	2267	b
575	3685	3704	3737	3682	c
676	4115	4133	4169	4111	c
800	4621	4662	4698	4641	a
1200	5947	6066	6113	6083	a
1500	6778	6953	7161	6983	a

(a) Johnston and Grilly, (1942) (b) Kestin and Leidenpost (1959

(c) Trautz Molstor and Zink, (1930)

mation on the Chapman-Enskog theory (Hirschfelder, *et al.*, 1954). It may be seen that the force constants determined in the present work from the second virial coefficient can represent the thermal conductivity of argon almost as satisfactorily as those determined from viscosity.

TABLE VI

Experimental and calculated values of the thermal conductivity K (in 10^{-7} cal. cm^{-1}. sec^{-1}. deg^{-1}.) for argon.

T °K	Expt (a)	Calculated from our force constants	Calculated from force constants of Michel, *et al.*	Calculated from force constants from viscosity
90.23	141	139	140	137
194.7	293	295	298	292
273.2	394	395	399	392
373.2	506	505	509	504
491.2	614	618	623	619
579.2	684	694	700	696

(a) Kannuluik and Carman, (1952)

CONCLUSIONS

(1) A consideration of the equilibrium properties of argon lends support to the suggestion of Kihara that the potential bowl of the spherical molecules should be wider than that given by the $L-J$ (12 : 6) model. The fact that the high temperature transport properties require a value of index of repulsion higher than 12 may be due to the inadequacy of inverse power repulsion at higher temperature. Hence at moderate temperature a $L-J$ (9 : 6) model may possibly give a better representation of the potential field, than a $L-J$ (12 : 6) potential.

(2) The set of force constants obtained on the $L-J$ (12 : 6) potential in this paper gives a more consistent representation of the various properties of argon than those hitherto obtained.

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APPENDIX

The values of B^* and $T^* \dfrac{dB^*}{dT^*}$ on the $L-J$ (9 : 6) model were obtained graphically from the table given by Epstein and Hibbert (1952). The values thus obtained are given in Table VII. This table may be used to calculate the Joule-Thomson Coefficient at zero pressure on the $L-J$ (9 : 6) model.

TABLE VII

Table for B^* and $B_1^* = \frac{dB^*}{dT^*}$. T^* for calculating μ^0, the zero-pressure Joule-Thomson Coefficient on L—J (9 : 6) model

T^*	B^*	B_1^*	T^*	B^*	B_1^*
0.5	−11.19	17.25	3.1	−0.355	1.085
0.55	− 9.40	16.51	3 2	−0 322	1.043
0.60	− 7.94	13.80	3 3	−0.275	1.010
0 65	− 6.98	11.70	3.4	0.248	0.975
0.70	− 6.17	10.15	3 5	−0.220	0.940
0.75	− 5.52	9 00	3.6	−0.188	0.923
0.85	− 4 52	7.31	3.7	−0 163	0.882
0 90	− 4 04	6.58	3.8	−0.134	0.857
0.95	− 3.74	6 03	3 9	−0 110	0.835
1 0	− 3.46	5 3	4 0	−0 085	0 810
1.1	− 2 97	4.62	4 1	−0.068	0.788
1.2	− 2.56	4.03	4.2	−0 052	0.765
1.3	− 2 25	3.62	4.3	−0.033	0.740
1.4	− 2.00	3.23	4 4	−0.017	0.72
1 5	− 1.78	2.91	4.5	−0.002	0.695
1 6	− 1 58	2.69	4.6	+0.012	0.680
1.7	− 1 42	2.49	4.7	+0.028	0 665
1.8	− 1 29	2.29	4 8	+0.042	0.650
1.9	− 1 15	2 12	4 9	+0.053	0.638
2.0	− 1.05	1.96	5.0	+0.063	0.620
2.1	− 0 958	1.84	6.0	+0.161	0.568
2.2	− 0.868	1.702	7.0	+0.23	0 426
2.3	− 0.787	1.602	8.0	+0.28	0.356
2.4	− 0 714	1 502	9.0	+0.317	0.302
2.5	− 0.646	1 410	10.0	+0.346	− 0.245
2.6	− 0.585	1.338	11.0	+0.365	0.187
2.7	− 0 530	1 27	12.0	+0.381	0.150
2.8	− 0.477	1.21	13.0	+0.395	0.104
2.9	− 0.435	1.165	14.0	+0.405	0.084
3 0	− 0.390	1 11	15.0	+0.416	0.0675